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Enabling Technologies for the Rapid Dechlorination of Polychloroarenes and PCBs

Giancarlo Cravotto,*[†] Davide Garella,[†] Lara Beltramo,[†] Diego Carnaroglio,[†] Stefano Mantegna,[†] and Carlo Maria Roggero.[‡]

† Dipartimento di Scienza e Tecnologia del Farmaco, Università di Torino, Via P. Giuria 9, Torino 10125, Italy.

‡ Sea Marconi Technologies, Via Ungheria 20, 10093 Collegno (TO), Italy.

*E-mail: giancarlo.cravotto@unito.it; Fax: +39 011 6707687; Tel: +39 011 6707684

Abstract

Dielectric heating and acoustic cavitation (ultrasound or high-performance disperser) may all dramatically enhance conversion rates and yields in heterogeneous metal-assisted organic reactions even when low reagent excesses are used. These so called "enabling technologies" bring with them process intensification, safer protocols, cost reduction and energy savings. We herein describe a series of rapid polychlorinated aromatic and PCBs dechlorinations (15 min) carried out in a moderate excess of metallic sodium and using non-conventional techniques. We compared the results with those obtained for reactions carried out under conventional heating and with those performed with less reactive metals such as magnesium and zinc. In this comparison, high-intensity ultrasound stands out as the technique of choice.

KEYWORDS. Polychloroarenes, PCBs, Dechlorination, Ultrasound, Microwaves, High-performance disperser.

1. Introduction

Reductive dechlorination has become one of the most attractive topics in chemistry since the Stockholm Convention on Persistent Organic Pollutants (POPs) imposed the elimination of polychlorinated biphenyls (PCBs) use by 2025 and their disposal via environmentally sound waste management by 2028. Besides incineration or high temperature pyrolysis, which are powerful but controversial elimination methods, there are several non-combustion alternatives to be considered. These are reported in Table 1. Of the several dechlorination methods available, the metal based process has been singled out as the most cost effective and efficient because no toxic by-products (i.e. biphenyl, phenylcyclohexadiene, and phenylcyclohexene) are formed. Nevertheless, safety concerns have been voiced over the huge metal excess that is usually required. Alkaline-earth metals (Ca, Mg) and transition metals (Ni, Pd, Fe, Ti and Zn) (Mitoma et al., 2004; Upendra and Suresh, 2008; Azzena et al., 2010; Liu et al., 2009; Zhang et al., 2011; Zhang, 2003; Fuku et al., 2010; Feng and Lim, 2005) have been investigated as alternatives to the alkaline metals (mainly Na) that are normally used. The reaction times of PCB dechlorination are in the region of several hours or even days. The use of alternative energy sources, such as microwaves (MW) (Kappe, 2004), ultrasound (US) (Cravotto and Cintas, 2006) or mechanochemistry (Nasir and Varma, 2012; Stolle

et al., 2011) has been proven to strongly accelerate the reductive process and limit gaseous emissions (Tajik et al., 2012; Liu et al., 2011; Zhang and Hua, 2000; Sáez, 2011).

Table 1. Non-combustion technologies for PCBs degradation.

METHOD	CHARACTERISTICS	Ref.
Reduction with alkali-metals	• Metal stability is a crucial factor (i.e. Ca *vs* Na) • Mild conditions (r.t., N_2 atmosphere) • Improved by catalysts (i.e. Pd/C, $TiCl_4$, $CoCl_2$, $Ni(OAc)_2$)	Chiu, *et al.*, 2012; Noma, *et al.*, 2003.
Base-catalyzed decomposition	• Cost-effective and safe dechlorination occurs with alkali hydroxides	Takada, *et al.*, 1997; Sun, *et al.*, 2007; Ye, *et al.*, 2011.
Catalytic hydro-dechlorination	• Heterogeneous catalysts (i.e. Fe, Ni, or Pd) and H_2 pressure • Aqueous or organic solvents • Generation of biphenyls, HCl	Schüth and Reinhard, 1998.
Photochemical - electrochemical processes	• Closed systems, mild and eco-friendly conditions • Safe additives (i.e. 2-propanol)	Hawarl, *et al.*, 1992; Noma, *et al.*, 2002; Ghosh, *et al.*, 2012.
Plasma arc	• High efficiency • Environmentally friendly • Generation of H_2O_2, H_2, O_2, O_3 (also radicals) • Shock waves and UV light may occur simultaneously • Mandatory energy control	Du, *et al.*, 2005.
Microbial reductive transformation	• Temperature, pH, substrate composition monitoring for microorganisms growth • Slow process	Borja, *et al.*, 2005; Field and Sierra-Alvarez, 2008.

The use of metal particles in a MW oven can result in arcing and generate fire or explosion if a flammable solvent is present. It is, however, possible to perform organic reactions using well-dispersed

fine metal particles in a high-boiling-point polar solvent. Whittaker and Mingos described all the safety operations needed to minimize the risk of arcing which include moderating the power rating, using low metal loads and ensuring efficient stirring (Whittaker and Mingos, 2000). Kappe showed, for the first time, how the electric field strength could influence the outcome of a chemical reaction. In low field density conditions, the metal undergoes a cleaning effect and becomes more reactive, whereas under a more intense electrostatic discharge the high temperature reached generates a carbonaceous material that covers the metal, thus reducing its effect (Gutmann et al., 2011). Besides the close control of electric field strength, another method that can influence this type of reaction is the use of an inert atmosphere (N_2 or Ar_2 pressure). This provides a totally safe environment in which to carry out the procedure as it avoids the risk of combustion and explosion in all MW reactions that use metals in a pivotal role (Cintas et al., 2012). US has found several applications in metal-assisted reactions (Cintas et al., 2011) and in heterogeneous conditions (Cravotto et al., 2003; Palmisano et al. 2011).

High-intensity US induces strong acoustic cavitation and streaming which enable efficient mixing, metal surface activation and particle dispersion to occur (Cravotto and Cintas, 2006). In the present study we intend to show how US, MW and high-performance

disperser favor the rapid metal-assisted dechlorination of polychloroarenes and PCBs.

2. Materials and methods

2.1. Materials

All the chemicals were used as received. 1,3,5-trichlorobenzene (<99%) and hexachlorobenzene were purchased from Fluka Chemika, 2,4-dichlorophenol (99%) and a sodium dispersion 30 wt% in toluene (<0.1mm particles size) were purchased from Acros Organics. Sodium cubes (99.95%), magnesium chips (98%) and Zn powder were purchased from Sigma-Aldrich. PCBs oil: (Askarel by Monsanto) a mixture of Aroclor 1260 70% and trichlorobenzene 30%. The US probe system (21.1 kHz, max power 250 W, Ø = 2.92 cm) with a titanium horn is commercially available from Danacamerini s.a.s. (Turin, Italy). MW-assisted reactions were carried out under pressure in a SynthWAVE by Milestone (Bergamo, Italy). An Ultra Turrax® T 25 Basic by IKA was used as the high-performance disperser.

2.2. Gaschromatography Analysis

a) Polychloroarenes; gaschromatography-mass spectrometry (GC-MS) analyses were performed in a Agilent 6890 gaschromatograph (Agilent Technologies - USA) fitted with a Agilent Network 5973 mass detector using a 30 m long capillary column, an i.d. of 0.25 mm and a film thickness of 0.25 μm.

GC conditions were; injection split 1:20, injector temperature 250°C, detector temperature 280°C. Gas carrier: helium (1.2 mL/min), temperature program; from 70°C (2 min) to 300°C at 5°C/min.

b) PCBs; Gaschromatography-electron capture detector (GC-ECD) analyses were performed in a Agilent 6890 gaschromatograph (Agilent Technologies - USA) fitted with an ECD, using a 50 m long 5% phenylpolysiloxane capillary column, i.d of 0.20 mm and film thickness 0.33 µm. Gas carrier; helium (1 mL/min), make-up gas for ECD; argon-methane (5%). ECD temp. 340°C. Splitless injection 1 µL. Temperature program: from 120°C (1 min), then 50°C/min up to 200°C (1 min); 5C°/min up to a 270°C; 20C°/min up to 315°C.

2.3. MW under pressure

Aryl halide (0.1 mmol, 1 eq), metallic reagent (15 eq of metal for each Cl atom) and toluene (10 mL) were placed in the reaction vessel. The mixture was irradiated with MW (average power 300 W) at 130°C for the optimized time of 15 min under N_2 pressure (5 bar). The solution was filtered on a Celite® pad, soaked in ethanol to remove any un-reacted sodium and analyzed by GC-MS.

2.4. US and the high-performance disperser

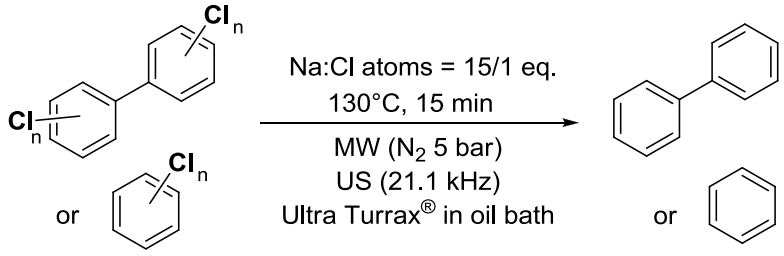
Aryl halide (0.1 mmol, 1 eq), the metallic reagent (15 eq of metal for each Cl atom) and hexadecane (10 mL) were placed in a three-necked-round-bottomed flask. The mixture, pre-heated in an oil bath at 130°C until the sodium melted, was then sonicated with an

immersion horn (21.1 kHz, 60W) for 15 min. In an alternative procedure, a high-performance disperser probe was inserted into the flask and switched on/off intermittently every minute for a total time of 30 min (15 min high speed mixing and 15 min pause) to avoid super-heating and damage to the Ultra Turrax®. The solution was filtered on a Celite® pad, soaked in ethanol to remove any un-reacted sodium and analyzed by GC-MS.

3. Results and discussion

In this paper, enabling technologies have been applied to the dechlorination process with the aim of designing a safe, fast and efficient protocol in the presence of a low alkali-metal excess (≤ 15 eq.). Four different techniques have been applied; MW, US, high-performance disperser (Ultra Turrax®) and simple conductive heating in an oil bath (OB) was used as a conventional method reference. The three main parameters that affect the dechlorination rate were; temperature, mixing efficiency and metal/chlorine atom ratio (scheme 1).

Scheme 1. Reductive dechlorination with non-conventional techniques.



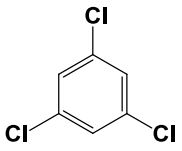
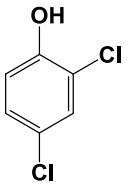
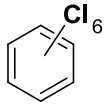
In this work, dechlorination reactions were carried out by suspending the reducing metal (mainly Na, 15 eq. for each Cl atom) in toluene or a hexadecane solution containing a polychloroarene. The first set of experiments was conducted with trichlorobenzene, 2,4-dichlorophenol and hexachlorobenzene.

MW-assisted dechlorination reactions were performed in a closed MW reactor (SynthWAVE - Milestone) under nitrogen pressure (5 bar) thus avoiding any possible risk of fire and explosion. The high power density (1.5 kW per 1.5 l) and the efficient cooling system enabled fast volumetric heating and rapid cooling with very sharp temperature ramps.

Table 2 reports the results achieved for MW-assisted reactions according to the varying conditions and sodium source (sodium cubes or a dispersion 30 wt% in toluene). In the light of the results obtained in a few preliminary experiments with 10 eq. (entry 5), we decided to proceed with a metal excess of 15 eq. for each Cl atom. Although the reactions proceed well in 30 minutes at 150°C (entries 1, 10 and 17), we also investigated milder conditions at the same reaction time. Complete dechlorination was also achieved (entries 2, 11 and 18) when the reaction was carried out at 130°C, whilst no reaction occurred within the 30 min period at temperatures below the metal melting point (entries 9, 16 and 23). However, the sodium dispersion showed much higher reactivity than the sodium cubes when the temperature was close to the metal melting point

because of its higher particle dispersion (entries 8, 15 and 22). A temperature of 130°C together with a sodium/chlorine atom ratio of 15 eq. and an average reaction time of 15 min was the best compromise in the case of MW-promoted reactions. Lower dechlorination yields were detected working under reflux in an OB (entry 3, 12 and 19).

Table 2. Residual polychloroarenes after MW-promoted dechlorination with Na (15 eq.) in toluene (5 bar N_2 pressure).

Entry	Substrate[#]	Time (min)	Temperature (°C)	Na cubes (residual %)	Na dispersion (residual %)
1		30	150	0	0
2		30	130	0	0
3		30	OB reflux	67	60
5		30	130	14[*]	10[*]
6		15	130	0	0
7		7	130	55	54
8		30	100	80	0
9		30	80	100	100
10		30	150	0	0
11		30	130	0	0
12		30	OB reflux	52	44
13		15	130	0	0
14		7	130	13	17
15		30	100	33	0
16		30	80	100	100
17		30	150	0	0
18		30	130	0	0
19		30	OB reflux	100	96
20		15	130	0	0
21		7	130	85	56
22		30	100	100	78
23		30	80	100	100

[#] In the cases of incomplete conversion, GC-MS analysis did not detect partially dechlorinated compounds; results are the mean of at least 2-3 trials

[*] Na 10 eq.

The optimization of the MW-assisted procedure caused a decrease in reaction time to 15 (entries 6, 13 and 20) and 7 min (entries 7, 14 and 21), where the former is the preferred choice. This study has provided us with the following order of reactivity; 2,4-dichlorophenol >> 1,3,5-trichlorobenzene > hexachlorobenzene. The last in the list was the most refractory towards dechlorination. The MW-assisted procedure was employed in experiments carried out with US (average power of 80 W) and with high-performance dispersers (Ultra Turrax® at 10,000 rpm). Both methods generate cavitation phenomena and cause the reactive metal to be very finely dispersed. Moreover they played a pivotal role in the set up of this protocol ensuring the process was strongly accelerated. Since the experiments were carried out at atmospheric pressure and at 130°C, toluene was replaced with hexadecane. A constant hexadecane solution reaction temperature was guaranteed by a thermostatted bath (130°C). At this temperature, the metallic sodium (cubes) melted (97.7°C) and therefore easily dispersed into the medium, however, particle size was a crucial point for the other metals (zinc and magnesium). Melting proceeded even more quickly when a commercially available sodium dispersion was used (30 wt% in toluene, < 0.1mm particles size). Table 3 shows the results achieved with the sodium dispersion, zinc and magnesium. The sodium dispersion gave excellent yields, confirming the results

obtained with the MW protocol. The yields were significantly lower in the presence of magnesium and zinc as they act in the solid phase.

Table 3. Residual polychloroarenes after treatment with US or a high-performance disperser with various metals (15 eq.) in hexadecane for 15 min at 130°C.

Entry	Method[#]	Substrate	Residual %		
			Na dispersion	Mg	Zn
24	US	trichlorobenzene	0	91	92
25		2,4-dichlorophenol	0	83	76
26		hexachlorobenzene	0	100	100
27	*Ultra Turrax®	trichlorobenzene	0	92	95
28		2,4-dichlorophenol	4	90	88
29		hexachlorobenzene	10	100	100

[#] Results are the mean of 2-3 trials

* Alternatively on/off 1 min (15 min high speed mixing and 15 min pause).

The optimized procedures; MW carried out in a pressurized reactor, high-intensity US with an immersion horn and the high-performance disperser (Ultra Turrax® at 10,000 rpm) were also tested in the dechlorination of PCBs. A mineral oil containing 271 ppm of PCBs was used to this aim and was treated with a sodium dispersion at 130°C for 15 min with all techniques. After a few preliminary experiments we defined a sodium excess value of 40 mole eq. as being optimal. Table 4 summarizes the results achieved; 7 ppm with MW, <2 ppm with US, 28 ppm with Ultra Turrax®, whilst the reference reaction in an oil bath gave a 120 ppm residue. All the reactions were monitored via GC-ECD.

Table 4. Residual PCBs in mineral oil (271 ppm) under OB, Ultra Turrax®, MW and US.

Entry	Method	Time (min)	PCBs residual (ppm) Na (15 mole eq)	PCBs residual (ppm) Na (40 mole eq)
30	oil bath	60	270	120
31	*Ultra Turrax®	15	79	28
32	MW	15	56	7
33	US	15	48	<2

*alternatively on/off 1 min (15 min high speed mixing and 15 min pause).

4. Conclusion

In conclusion, we have herein reported a dechlorination protocol performed under non-conventional techniques that enables a moderate excess of metallic sodium to be used rather than the much higher excesses that are currently commonplace. On the basis of the three main parameters studied, temperature, metal/chlorine ratio and physical activation, we can conclude that the crucial issues in the effectiveness of the procedure are the use of melted metal, a reasonable sodium excess and efficient physical metal activation/dispersion. Rapid reactions in low metal excesses (15 mole eq and 40 eq. for PCBs) are possible thanks to the enabling technologies we have outlined above and would be impossible under conventional heating.

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